PENTAFLUOROPROPANES AND HEXAFLUOROPROPANES AS WORKING FLUIDS FOR POWER GENERATION

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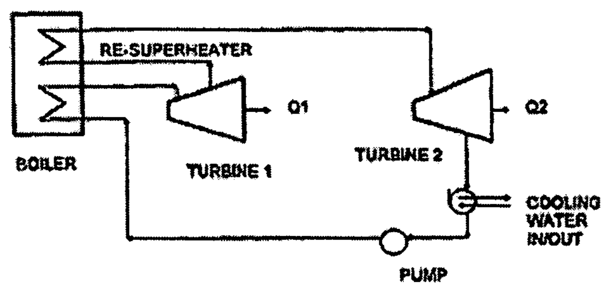
Abstract of **WO9806791**

A method for extracting mechanical energy via a Rankine cycle using hydrofluorocarbons. In particular, the invention concerns method for extracting mechanical energy via a binary Rankine cycle using pentafluoropropanes and hexafluoropropanes as working fluids for the secondary stage fluid. The system derives its energy from the temperature difference between a low grade thermal source, such as exhaust steam from a turbine, and a high quality low temperature source such as a water near its freezing point, for maximum efficiency.



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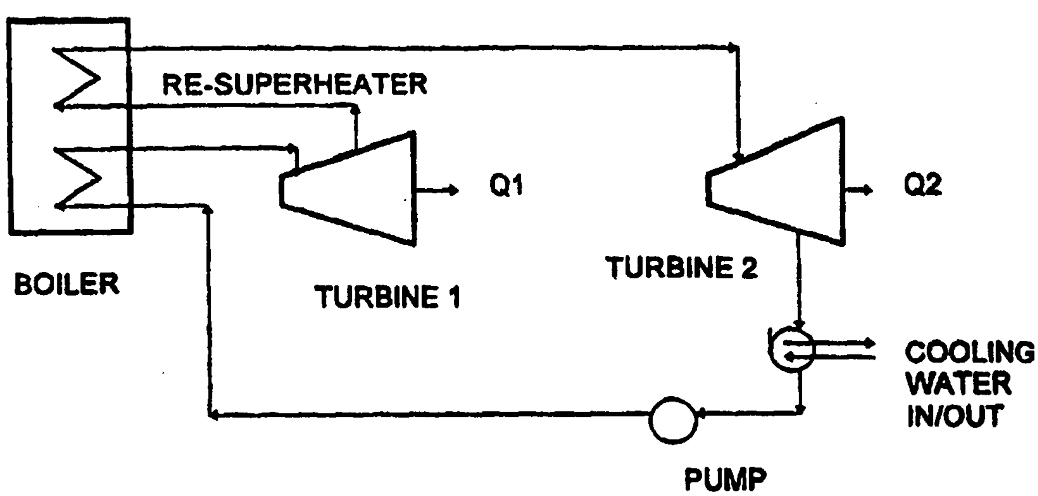

(57) Abstract

A method for extracting mechanical energy via a Rankine cycle using hydrofluorocarbons. In particular, the invention concerns method for extracting mechanical energy via a binary Rankine cycle using pentafluoropropanes and hexafluoropropanes as working fluids for the secondary stage fluid. The system derives its energy from the temperature difference between a low grade thermal source, such as exhaust steam from a turbine, and a high quality low temperature source such as a water near its freezing point, for maximum efficiency.

PENTAFLUOROPROPANES AND HEXAFLUOROPROPANES AS WORKING FLUIDS FOR POWER GENERATION

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention pertains to a method for extracting mechanical energy via a Rankine cycle using hydrofluorocarbons (HFC's). In particular, the invention concerns method for performing work via a binary Rankine cycle using HFC's, especially HFC propanes as a secondary stage working fluid. The system derives its energy from the temperature difference between a low grade thermal source, such as exhaust steam from a turbine, and a high quality low temperature source, such as a water near its freezing point, for maximum efficiency.

Description of the Prior Art

Water in the form of steam is the most commonly employed working fluid used to convert thermal energy into mechanical energy in Rankine cycle systems. This is due to its wide availability, low cost, thermal stability, nontoxic nature and wide potential working range. However, water has a high boiling point, high critical pressure and low density, all of which limit the obtainable power. Furthermore, the use of steam requires superheating and resuperheating to prevent condensation in a turbine. Condensation results in erosion of turbine parts and loss of overall efficiency. Other fluids have been used in certain power generation applications. Ammonia has been used in Ocean Thermal Energy Conversion (OTEC) systems and CFC-113 has been used to recover energy from waste heat such as exhausts from gas turbines.

It is also known to employ two working fluids in hybrid or binary power cycles. In such systems, water is used in a high temperature, high pressure first stage and a more volatile fluid is used in a cooler second stage. This arrangement can be more efficient than when only water and steam are employed.

In steam power plants, water is heated in boilers to produce high pressure, high temperature steam. The steam is then expanded through turbines, which drive motors, pumps, compressors and/or electrical generators. The steam does work on the turbine by transferring some of the energy that was used to heat and vaporize the water in the boiler to the device that the turbine rotates. The remainder of the energy that was transferred to the steam must be dumped into a "cold" reservoir, such as the earth's atmosphere, via cooling towers, or into rivers, lakes and oceans. In general, more than 50 % to 60 % of the energy used to boil the water must be dumped into the cold reservoir due to thermodynamic considerations. In plants where co-generation is not employed, an average of 40 % of the heat imparted to the steam is converted into mechanical work, with the remainder being wasted. Although not all of this heat energy can be put to use, wasted, low grade heat is a heretofore under-utilized energy resource.

It is known that if another working fluid is employed in the place of steam in a second stage, lower pressure turbine using the steam exiting from the higher pressure turbines to heat this second stage fluid and convert it from a liquid to a vapor, greater mechanical power output can be obtained from the same quantity of energy that was imparted to the steam. This translates into greater energy efficiency for the power plant, with potential lower overall operating costs. Increased efficiency can be achieved when a working fluid is chosen which is compatible with the power plant's operating conditions and which is also suitably paired to the temperature of the "cold reservoir". In this regard, a large body of very cold water, preferably near the freezing point of water can be used more effectively than warmer water as a cold reservoir resource. Such resources are often found in cold climates where there is a significant demand for electricity,

Certain halocarbons have been suggested as working fluids in power cycle arrangements. For example, U.S. patent 3,282,048 teaches the use of 1-bromo-2,2,2-trifluoroethane. U.S. patent 5,441,659 teaches azeotropic mixtures including an amine having the formula $N(CF_3)_a(CHF_2)_b(CH_2F)_c$ wherein a+b+c=3 and a

hydrofluorocarbon. U.S. patent 5,433,880 teaches power fluids which are azeotropic mixtures of sulfur containing compounds and a hydrofluorocarbon.

It would be desirable to have hydrofluorocarbon based working fluids which offer efficient use in heat pump and energy generation applications. Fluorocarbon based working fluids are considered to be environmentally safe substitutes for the presently used fully halogenated chlorofluorocarbons. The substitute materials should have the beneficial properties of chemical stability, thermal stability, low toxicity, non-flammability, and efficiency in-use, while at the same time not posing a risk to the planet's atmosphere. Furthermore, the ideal hydrofluorocarbon should not require major engineering changes to conventional technology currently used with CFC materials. It should also be compatible with commonly used and/or available materials of construction. According to the present invention, it has been found that certain HFC propanes have thermodynamic properties that allow their use as working fluids in a variety of applications. These propanes are particularly useful in thermal energy to mechanical energy conversion processes based on a Rankine cycle process due to their temperature and entropy characteristics, low boiling point, low latent heat of vaporization, low toxicity, negligible flammability and chemical stability. It has been found that certain hydrofluorocarbons, such as pentafluoropropanes, including HFC-245eb, HFC-245fa, HFC-245ea, HFC-245ca, and hexafluoropropanes such as HFC-236fa, HFC-236eb, HFC-236cb and HFC-236ea will not adversely affect atmospheric chemistry and have useful power cycle characteristics.

SUMMARY OF THE INVENTION

The invention provides a method for converting heat energy to mechanical energy which comprises heating a hydrofluorocarbon fluid having a boiling point at atmospheric pressure in the range of from about -5 °C to about 40 °C, to a temperature sufficient to form a pressurized vapor of the hydrofluorocarbon, and then causing the heated vapor to perform work.

The invention also provides an improved binary power cycle comprising a primary power cycle and a secondary power cycle, wherein high temperature steam is a primary working fluid in the primary power cycle, the improved method comprising employing a hydrofluorocarbon as the secondary working fluid by converting heat energy to mechanical energy by heating a hydrofluorocarbon fluid having a boiling point at atmospheric pressure in the range of from about -5 °C to about 40 °C, to a temperature sufficient to form a pressurized vapor of the hydrofluorocarbon, and then causing the heated, pressurized vapor to perform work.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a schematic representation of a power plant arrangement wherein a single fluid is used to convert power.

Figure 2 shows a schematic representation of a binary cycle power plant arrangement wherein two different working fluids can be used.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In industrial Rankine cycle thermal to mechanical energy conversion applications, the temperature and pressure of the steam generated and the arrangement of the turbines will vary, however, some common features exist in most power plants. Generally, more than one pressure range is employed, since an increased energy conversion efficiency is possible if the working fluids are employed in a binary cycle versus a single fluid (water) system. Very high pressure superheated steam is fed to a primary turbine, and lower pressure steam exiting from the primary stage is then fed to a lower pressure secondary stage turbine after being reheated. The exhaust steam from the secondary turbine still contains a considerable amount of energy in the form of the latent heat of vaporization. In situations where co-generation is employed, the thermal energy in the lower pressure steam is utilized for process heating; however, this is not feasible in many power plants due to location or lack of a need for some or all of the heat value in this steam. An example of such a plant arrangement is shown in Figure 1. Figure 1 shows a schematic representation of a typical power plant wherein a single fluid is

used to convert power. A boiler is used to superheat steam and the produced high temperature, high pressure steam is used to turn turbine 1 generating power Q1 Waste steam exits from turbine 1 at a lower temperature and pressure. This exiting steam is then re-superheated by the boiler and directed to turbine 2 which extracts additional power Q2. Steam exiting from turbine 2 is condensed by cooling water and directed back to the boiler for commencing the cycle again. In one embodiment of the invention HFC propanes can substitute for steam in such a single stage power cycle.

A more advantageous arrangement is a binary cycle power plant arrangement as shown in Figure 2. A boiler is again used to superheat steam and the produced high temperature, high pressure steam is used to turn turbine 1 to generate power Q1. Waste steam exits from turbine 1 at a lower temperature and pressure. This exiting steam is then used to heat and vaporize a second, different working fluid which is directed to turbine 2 and which extracts additional power Q2. Vapor exiting from turbine 2 is condensed by cold water and directed back to the secondary fluid heating stage for commencing the second stage again. In the most preferred embodiment of the invention steam is employed in the first stage and HFC propanes are employed in the second stage of such a binary power cycle. In an alternate embodiment, the heating of the hydrofluorocarbon is done with hot water or solar energy. The work is preferably done without substantial condensation of the hydrofluorocarbon. In a preferred embodiment, the pressurized hydrofluorocarbon vapor is cooled below its boiling point by cold water and then recycled by heating the hydrofluorocarbon to a temperature sufficient to form a heated pressurized vapor of the hydrofluorocarbon which is then caused to perform additional work.

One of the properties of HFC propanes that makes their use in heat to mechanical conversions advantageous is the entropy/temperature relationship at saturated vapor conditions. Heat energy can be converted to mechanical energy in a Rankine cycle in a process known as isentropic expansion. The entropy of the hydrofluorocarbon vapor increases as the heating temperature increases at vapor-liquid saturation equilibrium up to the critical point. As the gas at a higher temperature and pressure is expanded through a turbine to a region of lower pressure, it does work on the turbine, and exits

the turbine at a lower pressure and temperature. Entering pressures preferably range from about 250 psia to about 450 psia, and exiting pressures preferably range from about 5 psia to about 25 psia, depending on the coolant temperature, heat source temperature and HFC chosen. The difference in the enthalpies of the gas between the two points is equal to the amount of work that the gas does on the turbine. If the higher temperature, higher pressure gas has a decrease in its entropy as the temperature and pressure are lowered, the gas will not condense in an isentropic expansion. It will not partially liquefy as it drops in temperature and pressure across the turbine. Such condensation can cause unwanted wear and tear on the mechanical device (turbine), and can only be overcome by superheating the vapor prior to its entering the turbine. For small molecular species such as water, ammonia and CFC-12, superheating of the vapor is required to prevent significant condensation during an isentropic expansion. However, for larger molecules such as the pentafluoropropanes and hexafluoropropanes of this invention, the entropy increases as the temperature is raised in a saturated vapor, and condensation will not occur in an isentropic expansion.

In accordance with the invention, we have found that the fluids 1,1,2,2,3-pentafluoropropane (HFC-245ca), 1,1,1,2,3-pentafluoropropane (HFC-245eb), 1,1,2,3,3-pentafluoropropane (HFC-245ea) and 1,1,1,3,3-pentafluoropropane (HFC-245fa), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,2,2,3,3-hexafluoropropane (HFC-236ca), 1,1,1,2,2,3-hexafluoropropane (HFC-236cb) and 1,1,2,3,3,3-hexafluoropropane (HFC-236ea) and blends thereof are useful as energy conversion fluids. These high molecular weight hydrofluorocarbons have at least 70 weight percent fluorine. These compounds have favorable temperature, pressure, enthalpy, entropy characteristics as heat transfer materials. The normal boiling points of these materials range from about -5 °C to about 40 °C. The choice of which particular HFC would be used would be tailored to suit the temperature of the coolant available to the particular application. Blends of these materials could also be arranged, which would aid in customizing the working fluid to the particular application. Some of their properties are shown in Table 1.

Blends

TABLE 1

Properties of Pentafluorinated and Hexafluorinated HFC Propanes

COMPOUND		Boiling Point	Flash Point °C	Flame Limits vol. %
CF_2H-CF_2-CF_2H	236ca	10.0 °C	None	None
CF_3-CFH-CF_2H	236ea	6.0 °C	None	None
CF_3-CH_2-CF_3	236fa	-0.7 °C	None	None
CF_3-CF_2-CFH_2	236cb	-1.2 °C	None	None
CF_2H-CFH-CF_2H	245ea	39.3 °C	None	
CF_2H-CF_2-CFH_2	245ca	25.1 °C	None	
CF_3-CFH-CFH_2	245eb	22.7 °C	None	9.6 to 10.7
CF_3-CH_2-CF_2H	245fa	15.3 °C	None	

The present invention meets the need in the art for a working fluid which has a low ozone depletion potential and is a negligible contributor to greenhouse effect global warming compared with fully halogenated CFC materials, is effectively nonflammable, of low toxicity and is chemically and thermally stable in conditions where it is likely to be employed. These materials have the proper boiling points and thermodynamic characteristics that would be usable in power generation. They take advantage of some of the latent heat contained in low pressure steam which is presently not well utilized. Large quantities of low pressure steam can be found in numerous locations, such as in fossil fuel powered electrical generating power plants. Binary cycle processes using these HFC propanes would prove especially useful where a ready supply of a naturally occurring low temperature "reservoir", such as a large body of cold water, is available. The particular HFC fluid could be tailored to suit the power plant coolant temperature, maximizing the efficiency of the binary cycle.

The present invention is more fully illustrated by the following non-limiting Examples.

In the following examples, the increase in energy efficiency is demonstrated as compared to a model, described schematically in Figure 1, where only water/steam is

employed. The conditions of the steam entering the various points in the process are listed in Table 2. These have been chosen so that condensation does not occur in the turbines (expansion is isentropic), and only energy imparted to the steam in the boiler is considered. The combined theoretical energy output of the two turbines (Q1 + Q2) is 675.2 Btu/lb of steam, from 1693.8 Btu/lb. of steam, for an efficiency of 38.62 %.

TABLE 2

Conditions of Water/Steam in Model Power Plant

Position/Description	L Enthalpy Btu/lb.	Btu/lb.	V Enthalpy Btu/lb.	V Entropy °F
1. From Boiler, 1000 °F/1200 psia	na		1499.0	1.6289
2. From 1st Turbine, 325 °F/96 psia	295.5		1186.6	1.6059
3. From Reheater, 900 °F/60 psia	na		1479.0	1.9378
4. From 2nd Turbine, 126 °F/2 psia	na		1115.7	1.9240
5. From Condenser, 126 °F/2 psia	93.97		na	na
6. From Pump, 126 °F/1250 psia	97.6		na	na

The theoretical net power output $= Q1 + Q2 - \text{pump}$

$= (1499 - 1186.6) + (1479 - 1115.7) - 3.7$

$= 312.2 + 363.5 - 3.7$

$= 672.0$ Btu/lb. steam

Latent Heat of Vaporization @ 96 psia/328 °F = 891.1 Btu/lb.

Theoretical Heat energy input into steam $= (1499 - 97.6) + (1479 - 1186.6)$

$= 1693.8$ Btu/lb. steam

Theoretical energy efficiency $= 672.0/1693.8 = 39.67\ \%$

The example demonstrates the use of HFC-245 isomers and HFC-236 isomers in producing additional mechanical power from vapor that is exhausting from a steam powered turbine. In a typical facility, approximately 40 % of the thermal energy in the steam is converted into mechanical energy; the remainder must be sacrificed due to

thermodynamic considerations. The HFC materials would be circulated through their own reboiler/turbine/condenser system, extracting thermal energy from the exhaust steam while serving as the condensing fluid for the exhaust steam according to the schematic shown in Figure 2. Some of the relevant thermodynamic data employed in these examples is listed in Table 3.

TABLE 3

HFC Propane Thermodynamic Data

HFC Compound	Temp/[Press] °F/[psia]		L. Enthalpy Btu/lb.	V. Enthalpy Btu/lb.	V. Entropy Btu/lb. °F
HFC-245fa	300	[431]	na	148.396	0.2369
	70	[18.6]	28.923	110.753	0.2153
	70	[450]	29.933	na	na
HFC-245ca	300	[356]	na	154.265	0.2426
	70	[12.5]	28.208	114.233	0.2218
	70	[400]	29	na	na
HFC-245ea	300	[262]	na	161.437	0.2527
	100	[13.3]	36.148	129.831	0.2410
	100	[300]	37	na	na
	70	[6.7]	27.289	124.343	0.2407
	70	[300]	28	na	na
HFC-245eb	300	[378]	na	148.285	0.2354
	70	[13.9]	27.278	112.753	0.2187
	70	[420]	28	na	na
HFC-236fa	250	[405]	na	117.42	0.1969
	70	[38]	28.238	92.317	0.1802

70	[450]	29.2	na	na
40	[18.6]	19.623	87.20	0.1778
40	[450]	20.6	na	na

EXAMPLE 1

Condensed HFC-245fa at 70 °F and 18 psia is heated and vaporized to 300 °F and 431 psia by steam via a heat exchanger, employing saturated steam at 328 °F and 96 psia. Steam, exhausting from a high pressure turbine, with properties shown in Table 1, is sent to a heat exchanger, where it is condensed to a saturated liquid at 328 °F and 96 psia. This hot water is then pumped back through the boiler at 1250 psia to continue the water/steam cycle. The HFC-245fa that is vaporized by the latent heat rejected from the 96 psia steam condensing into 96 psia water is then passed through the low pressure turbine and condensed using cooling water at 45 °F. The theoretical work that the fluid could do on the turbine would be 37.6 Btu/lb. of HFC-245fa, while the heat required to boil the fluid would have been 118.5 Btu/lb. After subtracting 1 Btu/lb. required to pump liquid HFC-245fa to 450 psia, the theoretical efficiency would be 31.24 %. The amount of HFC-245fa that is heated/boiled is 7.52 lbs. per lb. of saturated steam that is condensed, and the theoretical amount of work extracted from each lb. of steam condensed (at 891.1 Btu/lb. of latent heat of condensation) is (7.52)(36.633), or 275.4 Btu per lb. of steam. The combined steam/HFC-245fa output is 587.8 Btu/lb. from 1203.5 Btu/lb. steam, or 0.4884 Btu mechanical per 1.0 Btu thermal input. These results are shown below:

Efficiency, HFC-245fa cycle only	= 31.24 %
Net mechanical energy/lb. HFC-245fa	= 37.6 Btu/lb.
Thermal input into HFC-245fa/cycle	= 118.5 Btu/lb.
Work done on HFC-245fa - pump	= 1.01 Btu/lb.
Lbs. HFC-245fa/lb. steam	= 7.52
Net work output/lb. steam	= 275.4 Btu/lb.
Total Binary cycle work output	= 587.8 Btu/1203.5 Btu thermal = 0.4884 : 1

Efficiency increase versus model = 0.4884/0.3967

= 1.23, or a 23 % increase

As a comparison, the power output from the two turbine approach using re-superheated steam would be 687.2 Btu/lb. from 1779.2 Btu/lb., or 0.3967 Btu mechanical per Btu of thermal energy. The energy gain using the binary combination would be found by dividing 0.4884 by 0.3862, or 1.23. Thus, a 23 % increase in work is accomplished with the binary system for the same quantity of fuel used to power the single working fluid system.

EXAMPLE 2

HFC-245ca is used as the secondary working fluid, with the thermodynamic conditions described in Table 3. The 70 °F liquid is converted into saturated vapor at 300 °F and 356 psia with the same quality steam as in Example 1, then sent through a turbine and condensed using 45 °F cooling water. The results of the similar calculations are as follows:

Efficiency, HFC-245ca cycle only	= 31 31%
Net mechanical energy/lb. HFC-245ca	= 39.21 Btu/lb.
Thermal input to HFC-245ca	= 125.235 Btu/lb.
Work done on HFC-245ca	= 0.822 Btu/lb.
Lbs. HFC-245ca vaporized/lb. steam	= 7.12
Net work output/lb. steam	= 279.2 Btu/lb.
Total Binary cycle work output	= 591.6 Btu/1203.5 Btu thermal
	= 0.4916 : 1
Efficiency increase vs. model	= 0.4916/0.3967
	= 1.24, or 24 % potential increase

EXAMPLE 3

In this example, Example 1 is duplicated where HFC-245ea is the working fluid in an environment where warmer cooling water is present (90 °F). The HFC is heated to 300 °F and 262 psia, then sent through a turbine and condensed to a 100 °F liquid. The results are as follows:

Efficiency, HFC-245ea cycle only	= 24.7 %
Net mechanical energy/lb. HFC-245ea	= 30.95 Btu/lb.
Thermal input into HFC-245ea	= 124.7 Btu/lb.
Work done on HFC-245ea - pump	= 0.654 Btu/lb.
Lbs. HFC-245ea vaporized/lb. steam	= 7.15
Net work output/lb. steam	= 221.2 Btu/lb.
Total Binary cycle work output	= 533.6 Btu/1203.5 Btu thermal
	= 0.4434 : 1
Efficiency increase versus model	= 1.12, or a 12 % increase

EXAMPLE 4

Example 1 is duplicated except HFC-245eb is employed as the secondary working fluid. Using the same steam conditions as in the previous examples and employing 45 °F cooling water to condense the HFC vapors to 70 °F The following results are noticed:

Efficiency. HFC-245eb cycle only	= 28.59 %
Net mechanical energy/lb. HFC-245eb	= 34.61 Btu/lb.
Thermal input into HFC-245eb	= 120.1 Btu/lb.
Work done on HFC-245eb - pump	= 0.926 Btu/lb.
Lbs. HFC-245eb vaporized/lb. steam	= 7.42
Net work output/lb. steam	= 256.8 Btu/lb.
Total Binary cycle work output	= 569.2 Btu/1203.5 Btu thermal
	= 0.4730 :1
Efficiency increase versus model	= 1.19, or a 19 % increase

EXAMPLE 5

In this example, HFC-236fa is the working fluid in a location where high quality cooling (at 35 °F) is available. The same steam conditions are employed, with the HFC leaving the steam heat exchanger at 250 °F at 405 psia (very close to the critical point of HFC-236fa) and condensing to 40 °F at 19 psia. The following results are noticed:

Efficiency, HFC-236fa cycle only	= 29.93 %
Net mechanical energy/lb. HFC-236fa	= 29.276 Btu /lb.
Thermal input into HFC-236fa	= 96.85 Btu/lb.
Work done on HFC-236fa - pump	= 0.944 Btu/lb.
Lbs HFC-236fa vaporized/lb. steam	= 9.20
Net work output/lb. steam	= 269.3 Btu/lb.
Total Binary cycle work output	= 581.7 Btu/1203.5 Btu thermal
	= 0.4833: 1

Efficiency increase versus model = 1.22, or a 22 % increase

EXAMPLE 6

In this example, HFC-236ea is employed as the Rankine cycle working fluid. The liquid 70 °F (at 26.1 psia) is pumped through a heat exchanger and raised to a vapor/supercritical fluid at 300 °F and 513 psia. It is then be put through a turbine and condensed with 45 °F cooling water into a liquid at 70 °F. In this example, the following apply:

Temperature	Enthalpy - (Btu/lb.)	Entropy - (Btu/lb. °F)
70 °F	liquid - 28.268	na
	vapor - 95.931	0.1871
300 °F	vapor - 128.37	0.2095

Efficiency	= 31.29 %
Net mechanical energy/lb. HFC-236ea	= 31.327 Btu/lb.
Thermal input into HFC-236ea	= 98.99 Btu/lb.
Work done on HFC-236ea - pump	= 1.112 Btu/lb.
Lbs HFC-236ea vaporized/lb. steam	= 9.00
Net work output/lb. steam	= 281.9 Btu/lb.
Total Binary cycle work output	= 594.1 Btu/1203.5 Btu thermal
	= 0.4936 : 1
Efficiency increase versus model	= 0.4936/0.3967
	= 1.24, or a 24.4 % increase

Note: For HFC-236ea Tc = 300 °F

Pc = 478 psia

Tb = 42.9 °F @ 1 atm. pressure

The above examples are a simplified representation of the use of turbines in a power plant to convert thermal energy into mechanical energy. It does not take into account the energy losses due to pumping condensed liquids through piping/heat exchangers/boilers, the complicated feedback loops used to prevent condensation impacting upon turbine blades, preheating systems and several other features of power plants. However, these losses are kept as small as is practical, and should not be more than 2 to 5 % of the total power output from the turbines. These calculations also do not take advantage of any heat value available as superheated vapor when the HFC's exit the turbine. Finally, it may be possible to adjust conditions so that water is allowed to exit the turbine at higher pressures, thus allowing for an increase in the temperature driving force and thus for improved Rankine cycle efficiencies.

The HFC compounds of this invention have several properties which are beneficial to power generation. These include low viscosity of these fluids which lowers pumping losses, large molecular weight of the compounds and corresponding high densities of the vapors compared to similar pressured steam, the low latent heat of vaporization and good heat transfer properties. Turbines that are designed to use these HFC materials would have a greater energy output per unit volume than a steam turbine at the same pressures. This is important, since low pressure turbines in large energy plants can be enormous in size as well as cost. Furthermore, at the temperatures cited in the above examples, thermal stability is good, especially with materials such as stainless steel SS 304 and steel which are commonly used turbine materials.

What is claimed is:

1. A method for converting heat energy to mechanical energy which comprises heating a hydrofluorocarbon fluid having a boiling point at atmospheric pressure in the range of from about -5 °C to about 40 °C, to a temperature sufficient to form a pressurized vapor of the hydrofluorocarbon, and then causing the heated vapor to perform work.

2. The method of claim 1 wherein the hydrofluorocarbon comprises at least 70 weight percent fluorine.

3. The method of claim 1 wherein the hydrofluorocarbon fluid comprises a mixture of two or more hydrofluorocarbons such that the mixture has a boiling point at atmospheric pressure in the range of from about -5 °C to about 40 °C.

4. The method of claim 1 wherein the hydrofluorocarbon is a pentafluoropropane.

5. The method of claim 1 wherein the hydrofluorocarbon is a hexafluoropropane.

6. The method of claim 1 wherein the pressurized hydrofluorocarbon vapor is subsequently cooled below its boiling point by cold water and then recycled by heating the hydrofluorocarbon to a temperature sufficient to form a heated pressurized vapor of the hydrofluorocarbon which is then caused to perform additional work.

7. The method of claim 1 wherein the hydrofluorocarbon comprises at least one nonflammable pentafluoropropane or hexafluoropropane whose vapor entropy under vapor-liquid equilibrium conditions increases as the temperature increases, has at least 70 weight percent fluorine; wherein the work is performed on a turbine with a

saturated vapor of the hydrofluorocarbon without substantial condensation of the hydrofluorocarbon; wherein the heating is done with steam, hot water or solar energy in a heat exchanger at a temperature of from about the boiling point of the hydrofluorocarbon or greater; wherein exhaust vapor of the hydrofluorocarbon from the turbine is subsequently condensed by cooling below its boiling point by cold water and then recycled by heating the condensed hydrofluorocarbon to a temperature sufficient to form a heated, pressurized vapor of the hydrofluorocarbon and then causing the heated, pressurized vapor to perform additional work on the turbine.

8. The method of claim 7 wherein the hydrofluorocarbon is selected from the group consisting of $CF_2HCFHCF_2H$(ea); $CF_2HCF_2CFH_2$(ca); $CF_3CFHCFH_2$(eb); $CF_3CH_2CF_2H$(fa); $CF_2HCF_2CF_2H$(ca); CF_3CFHCF_2H(ea); $CF_3CH_2CF_3$(fa); $CF_3CF_2CFH_2$(cb) and mixtures thereof.

9. In a binary power cycle comprising a primary power cycle and a secondary power cycle, wherein high temperature steam is a primary working fluid in the primary power cycle, the improved method comprising employing a hydrofluorocarbon as the secondary working fluid by converting heat energy to mechanical energy by heating a hydrofluorocarbon fluid having a boiling point at atmospheric pressure in the range of from about -5 °C to about 40 °C, to a temperature sufficient to form a pressurized vapor of the hydrofluorocarbon, and then causing the heated, pressurized vapor to perform work.

10. The method of claim 9 wherein the hydrofluorocarbon is selected from the group consisting of $CF_2HCFHCF_2H$(ea); $CF_2HCF_2CFH_2$(ca); $CF_3CFHCFH_2$(eb); $CF_3CH_2CF_2H$(fa); $CF_2HCF_2CF_2H$(ca); CF_3CFHCF_2H(ea); $CF_3CH_2CF_3$(fa); $CF_3CF_2CFH_2$(cb) and mixtures thereof.

INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9302150 A	04-02-93	AU 2343692 A	23-02-93
		CN 1068841 A	10-02-93
		DE 69204290 D	28-09-95
		DE 69204290 T	11-04-96
		EP 0595937 A	11-05-94
		EP 0661365 A	05-07-95
		ES 2078056 T	01-12-95
		HK 19496 A	09-02-96
		MX 9204265 A	01-02-93
WO 9422973 A	13-10-94	US 5538659 A	23-07-96
		EP 0692008 A	17-01-96
		JP 8508495 T	10-09-96
		US 5616275 A	01-04-97
WO 9615206 A	23-05-96	US 5558810 A	24-09-96
		EP 0792332 A	03-09-97
EP 0127365 A	05-12-84	AU 2839284 A	22-11-84
		DK 245884 A	21-11-84
		JP 60004582 A	11-01-85
		US 4541943 A	17-09-85
DE 3445785 A	19-06-86	DE 3619547 A	17-12-87
US 4324983 A	13-04-82	NONE	